THERMAL INVESTIGATION OF SYNTHESIS OF PEROVSKITE

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ABSTRACT

Perovskite is found in some contact metamorphosed impure limestone. Also it occurs as an accessory mineral in a wide variety of undersaturated rock types, including potassic lavas and alkali pyroxenites. Little is known concerning the thermal condition of formation of perovskite. The present work represents a thermal investigation of synthesis of perovskite by sintering of rutile with calcite in presence of graphite by using derivatograph. The data obtained indicate that complete sintering takes place at 970°C with the formation of orthorhombic perovskite. Also the results of the differential thermal analysis and *X*-ray diffractometric study of sintering products have been reported.

РЕЗЮМЕ

Нами был найден перовскит в некоторых загрязненных, метаморфозированных, известняковых образцах. Этот минерал также появляется в виде случайной компоненты в широком классе насыщенных пород, включительно калиевых лав и алкали пироксенитов. Нам мало известно относительно термических условий образования пероксита. В настоящей работе приводятся результаты по исследованию термических условий синтеза перовскита и кальцита при наличии графита. При этом нами был использован дериватограф. Данные указывают на то, что образование туфы имеет место при температуре 970°C и образуется ортохомбический перовскит. Результаты дифференциального термического анализа и дифрактометрического исследования с помощью X-лучей также приводятся.

Introduction

Perovskite occurs as an accessory mineral in basic and alkaline rocks and is often found as a deuteric mineral in such rocks, commonly in association with melilithe leucite or nepheline.

It has been recorded also from a diabase-porphyrite where it is considered to be pseudomorphous after ilmenite. Perovskite is found in some contact metamorphosed impure limestones, where often it occurs as the cerium or niobium-rich variety. At the dolerite limestone contact of Scawt Hill, Northern Ireland, perovskite occurs both in the hybrid rock formed by assimilation of carbonate and as a constituent of the exogenous contact zone, where it is associated with larnite, melilithe, spinel and wollastonite. (15).

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Little is known concerning the thermal condition of formation of perovskite. This present work reports a thermal investigation of synthesis of perovskite by sintering of rutile with calcite in presence of graphite by using derivatograph. Also, the results of the differential thermal analysis and *X*-ray diffractometric study of sintering products are reported.

Rutile and anatase did not give any thermal reaction during heating. At 200 – 900°C, perovskite lattice remains rhombic, but becomes more symmetrical. It fuses congruently at 1915°C. The thermogram of calcite shows a sharp and large exothermic peak at 880°C, which represents its dissociation to calcicoxide and liberation of carbon dioxide. Several data can be found on the thermal character of rutile, anatase, perovskite and calcite in the literature (1 – 9, 13, 14, 16, 17).

Experimental Work

This research was carried out with rutile concentrate, having chemical composition and X-ray analysis as given in tables (1) and (2) respectively.

Chemical composition of Rutile concentrate

Table (1)

Chemical component	Content, %
TiO_2	95.84
SiO_2	1.80
Al_2O_3	0.78
Fe_2O_3	0.61
V_2O_5	0.32
MnO	0.05

The studied rutile is reddish-brown in colour. Rutile is associated with some mineral impurities such as zircon, quartz, garnet, corundum, amphiboles and others in fine grains and in small amount. None of the contaminants was detected by *X*-ray analysis, therefore an individual mineral may be present as a major constituent which is in good agreement with the mineralogical study.

The *X*-ray analysis of the studied rutile, table (2) shows that its parameters of crystal lattice are consistent with literature data. The *X*-ray powder diffraction data of the used calcite are given in table (3).

Table (2)

X-ray powder diffraction data of rutile

d(Å) ASTM	d(Å) Observed	I ASTM	I Observed	h k l
3.25	3.249	100	100	1 1 0
2.477	2.487	50	50	1 0 1
2.297	2.297	8	6	2 0 0
2.188	2.188	25	25	1 1 1
2.054	2.053	10	9	2 1 0
1.687	1.689	60	58	2 1 1
1.624	1.626	20	20	2 2 0
1.480	1.481	10	10	0 0 2
1.453	1.453	10	9	3 1 0
1.360	1.362	20	22	3 0 1
1.347	1.349	12	12	1 1 2

Table (3)

X-ray powder diffraction data of calcite

d(Å) ASTM	d(Å) Observed	I ASTM	I Observed	h k l
3.86	3.863	12	11	1 0 2
3.035	3.035	100	100	1 0 4
2.845	2.843	3	3	0 0 6
2.495	2 493	14	16	1 1 0
2.285	2.284	18	22	1 1 3
2.095	2.095	18	18	2 0 2
1.927	1.926	5	6	2 0 4
1.913	1.913	17	18	1 0 8
1.875	1.875	17	22	1 1 6
1.626	1.626	4	4	2 1 1
1.604	1.604	8	9	2 1 2
1.587	1.586	2	1	1.0.10
1.525	1.524	5	5	2 1 4
1.518	1.518	4	3	2 0 8
1.510	1.509	3	2	1 1 9
1.473	1.472	2	2	2 1 5
1.440	1.440	5	(	3 0 0
1.422	1.423	3		0.0.12

Techniques of Work:

Starting materials are usually consisted of rutile mixes. Calcite and graphite are used in mixes in particular amounts. Mixes were processed by repeated grinding in an automated agate morter and sieving till all the powder pass through 0.06 mm sieve and pestle for one hour to achieve homogeneity.

Apparatus:

Experiments were carried out in ceramic crucible, heated in an electrical furnace under suction of carbon dioxide. The character of the reaction of sintering of rutile with calcite in presence of graphite was studied by thermal analysis using P a u l i k F., P a u l i k J. and E r d e y L. (MOM) derivatograph (11, 12). This apparatus records simultaneously four thermal curves: (T) the change of temperature of sample, (DTA) differential thermal analysis, (TG) thermogravimetric, (quantitatively in mg) and (DTG) derivative thermogravimetric one a single sample under controlled conditions. DTA and temperature measuring thermocouples are Pt/Pt-Rh wires. Ceramic crucible and a ceramic sample holder were used. Alumina, calcined at 1000°C, was used as a reference material. The parameters during tests were as follows: weight

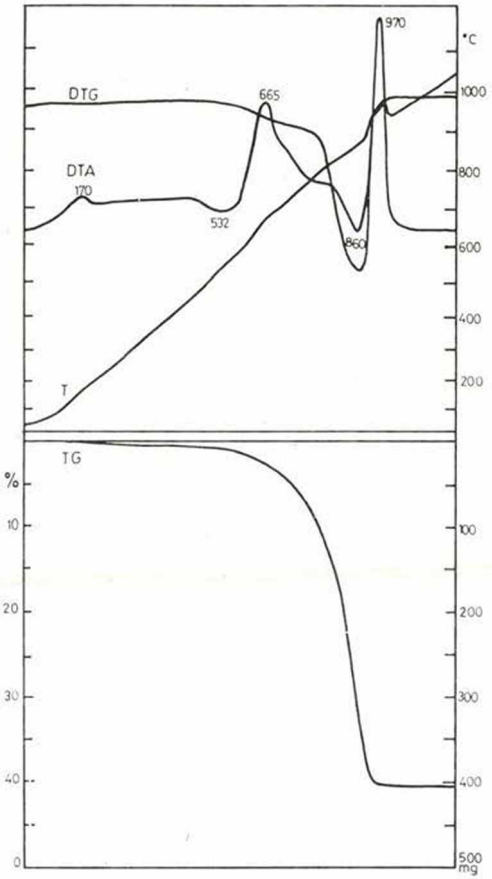

Fig. 1: Derivatogram of rutile sintering with calcite in presence of graphite. Weight of sample 1000 mg. Heating rate 10 °C/min.

of sample 1000 mg, T – 1200°C, DTA – 1/3, DTG – 1/5, TG – 500 mg and heating rate 10°C per minute. All determinations were carried out in an atmosphere under suction of carbon dioxide.

Phase Identification and Characterization:

The end products of sintering of rutile with calcite were studied both microscopically and by *X*-ray analysis. Perovskite is colourless to dark brown in thin section and has a very high relief, anisotropic.

X-ray Procedure:

A Siemens crystalloflex diffractometer was used with nickel filtered copper radiation. Exposure was one hour and scanning speed was 1° 20 per minute, at 1 cm per minute chart speed. Intensities were collected to maximum 20 = 65°. The sensitivity of the experiment, was 4×10^4 impl./min., and the statistical error was 1.5%.

Results and discussion

For studying the influence of rutile on the thermal behaviour of calcite, and the formation of perovskite, DTA experiments were carried out using calcite in amount 150% of theoretical value. The obtained derivatogram was evaluated on the basis of literature data with trial to explain the reactions which may be connected to certain peaks of DTA curve, and by comparing it with that of calcite and other components in the mix. The small and wide endothermic peak at 532°C may be due to the presence of some mineral impurities with rutile. The exothermic peak at 665°C may represent the burning of graphite and the combustion of volatiles. This is accompanied by ash arp decrease in weight (TG). The *X*-ray powder diffraction pattern shows the first appearance of perovskite above 665°C. The large endothermic peak at 860°C, represents the intensive dissociation of calcite and probably the reaction between the resulted calcium oxide and rutile. This process is connected with a remarkable decrease in weight (TG) due to the removal of carbon dioxide. According to the thermal curve of this mixture, the beginning of decomposition of calcite follows directly the end of exothermic reaction.

The sharp and large exothermic peak at 970°C may be due to the intensive reaction between rutile and the dissociated calcite. The reaction of formation of perovskite follows immediately the endothermic reaction of dissociation of calcite. The sinterting of rutile with calcite results in the production of orthorhombic perovskite. Its *X*-ray powder diffraction data are given in table (4). The *X*-ray data of synthetic mineral are consistent with those of natural perovskite.

Table (4)

X-ray powder diffraction data of Perovskite

d(Å) ASTM	d(Å) Observed	I ASTM	I Observed	h k l
3.824	3.826	14	20	1 0 1, 2 0 0
3.423	3.426	3	5	1 1 1
2.719	2.719	40	50	2 0 0
2.701	2.700	100	100	1 2 1, 0 0 2
2.563	2.565	1	2	2 1 0
2.428	2.430	1	2	2 0 1
2.413	2.412	2	4	1 0 2
2.313	2.308	4	6	2 1 1
2.303	2.304	7	10	0 3 1
2.217	2.219	6	9	2 2 0
2.201	2.204	4	8	0 2 2
2.121	2.123	2	4	1 3 1
2.050	2.049	2	4	2 2 1
2.040	2.043	1	2	1 2 2
1.911	1.911	50	80	0 4 0
1.860	1.883	2	2	2 3 0
1.856	1.858	3	4	2 1 2
1.757	1.784	1	1	2 3 1
1.752	1.752	1	1	1 3 2
1.746	1.748	1	1	0 1 3
1.719	1.719	2	3	3 0 1
1.710	1.712	3	5	2 2 2, 1 4 1
1.703	1.702	2	3	1 0 3
1.676	1.676	3	4	3 1 1
1.663	1.664	1	1	1 1 3
1.567	1.568	14	22	3 2 1
1.563	1.563	16	25	2 4 0
1.557	1.558	25	30	0 4 2
1.529	1.532	1	1	2 3 2
1.498	1.501	1	1	1 4 2, 2 0 3
1.470	1.475	1	2	0 5 1, 2 1 3
1.466	1.468	1	1	0 3 3

Determination of thermodynamic constants

Before studying the conditions of formation of perovskite from the reaction of rutile with calcite, an attempt was carried out for calculation of its thermodynamic constants. The following thermodynamic data were used in calculation: (ΔF°), standard free energy of formation of perovskite, rutile and calcium oxide are − 376.517, −212.559, and − 144.352 Kcal/mol. respectively.

The reaction of formation of perovskite from its components may be represented as:

$$TiO_2 + CaO \longrightarrow CaTiO_3$$

The standard free energy of the reaction:

$$\Delta F^{\circ}_{\text{reaction}} = \Delta F^{\circ}_{\text{perovskite}} - \Delta F^{\circ}_{\text{rutile}} - \Delta F^{\circ}_{\text{CaO}}$$
$$= -376.317 + 212.559 + 144.352$$
$$= -19.606 \text{ Kcal/mol.}$$

The equilibrium constant of the reaction may be calculated from the equation at 25°C:

$$\log K = \frac{-\Delta F^{\circ}}{4.575 \times 298} = -0.000733\, \Delta F^{\circ}$$
$$= 0.000\,733 \times 19\,606 = 14.371$$
$$K = 2.35 \times 10^{14}$$

The equilibrium constant is large and the reaction of formation of perovskite may thus be practically considered as irreversible.

For studying the effect of temperature on the efficiency of perovskite formation, some runs were carried out using rutile mixes with calcite in excess amount 50% and graphite 10% of rutile charge at different temperatures, ranging from 665.700 up to 970°C during two hours.

From the obtained result (Table 5), it is shown that the efficiency of titanate formation sharply increases with temperature. The products of sintering of these runs were identified both microscopically and by *X*-ray diffractometer. By microscopic examination of this reaction of the products of sintering at 665, 700°C considerable number of rutile grains were detected with few fine grains of perovskite. This gives good idea about the incomplete sintering. As the temperature of sintering increases, the amount of perovskite increases. At 970°C the reaction between rutile and calcite takes place completely. At such temperature only few relict grains were detected in matrix of perovskite.

Table (5)

Effect of temperature on sintering

Temperature, %	Efficiency of sintering, %
700	30.9
800	72.6
860	90.2
970	98.8

The *X*-ray powder diffraction pattern of the end product of sintering at 970 °C is shown in figure (2). It can be observed that rutile peaks completely disappeared in such product representing the complete sin-

tering. The *X*-ray peaks of perovskite are narrow and intense suggesting good crystallinity. The microscopic study of the product phases of rutile sintering with calcite is in good agreement with *X*-ray diffractometric study.

From the above mentioned thermal investigation, the reaction of sintering of rutile with calcite takes place completely at temperature above 860°C. The sintering results in the formation of orthorhombic perovskite.

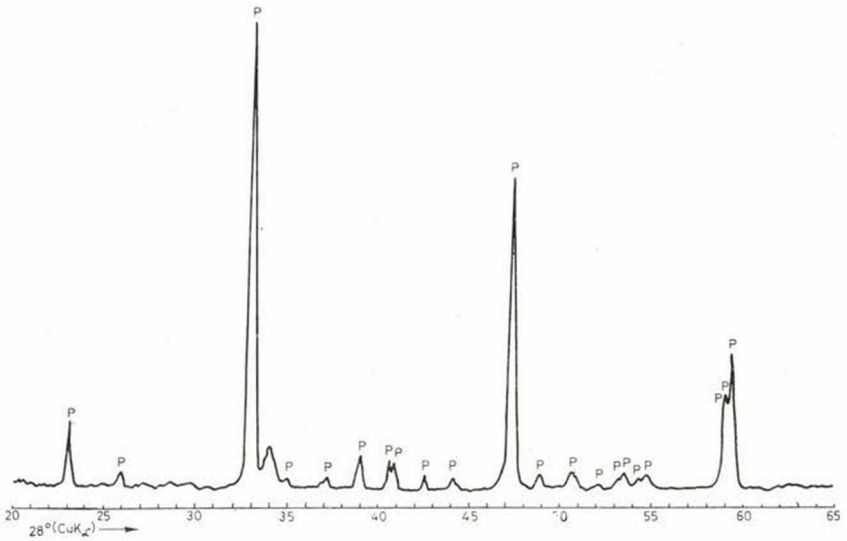

Fig. 2: *X*-ray powder diffraction pattern of the end product of sintering of rutile with calcite in presence of graphite at 970°C

Conclusion

The thermal study of the reaction between rutile and calcite has revealed that complete sintering takes place at 970°C with the formation of orthorhombic perovskite. Perovskite can also be formed at lower temperature above 700°C but it needs long time. The microscopic study and *X*-ray diffraction data of synthesised perovskite are in good agreement with the natural mineral.

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